



Cometary organic chemistry: a review from observations, numerical and experimental simulations

H. Cottin*, M.C. Gazeau, F. Raulin

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Universités Paris 7 and Paris 12, C.M.C., 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

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Abstract

This paper is a review dealing with the organic chemistry of comets. It describes how the chemical composition of comets can provide information about the chemistry of the interstellar medium, and the formation of the solar system. We discuss to what extent they could have brought to Earth the ingredients essential to the emergence of life: water and prebiotic compounds. We review all molecules which have been detected or tentatively detected in comets by remote sensing or in-situ observations, inputs of theoretical models, and all other organic species expected to be present from the results of experimental simulations. This compilation yields a list of more than a hundred molecules which can be used as a reference for the preparation of experiments developed for the Rosetta and Deep Space 4 cometary missions. We point out that further experiments are necessary to investigate the connections between the solid and gaseous phases of comets, especially studying the photodegradation of high molecular weight compounds which could be present in the nuclei. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Comets are often considered as the last witness of the formation of our solar system. One of the key points to study and understand, in the investigation of comets, is how much ice and dust particles, accreted in comets, have been altered in the solar nebula before, during and after the formation of the Sun, planets, and small bodies such as asteroids and comets. In other words, to what extent cometary matter is of interstellar or solar nebula origin. Moreover, it is now quite obvious that comets have brought to the Earth a certain amount of volatile compounds such as water, and other inorganic and organic compounds. But their relative contribution compared to the initial material incorporated during the Earth's accretion is still an outstanding issue. Finally, among those organic compounds imported by comets, it is thought that some of them may have contributed to the starting of the chemical evolution that allowed the appearance of life on Earth.

The aim of this paper is to review the current knowledge concerning the chemical aspect of cometary nuclei. It is essential to define the kind of organic materials that are likely to be detected during future missions of

cometary exploration, including in-situ measurements as well as close remote sensing observations. This will be the case for the ESA Rosetta mission and the NASA Deep Space 4 (DS4) mission. Such a compilation is necessary for preparation of in-situ experiments like Gas Chromatography analysis, which requires the selection and calibration of columns as a function of the nature and chemical family of the expected molecules. It is also an opportunity to raise new questions and start new experimental work to prepare for the interpretation of future results.

In the first part of this paper, we show why comets are of such interest and what information can be deduced from an accurate study of their composition. Next, we review all molecules already detected or tentatively detected by remote or in-situ observations. In the following section dealing with numerical simulations, the kind of information models can bring is discussed. Finally, we review experimental simulations, which predict the presence of many, as yet undetected, molecules to be present in comets.

2. Why study the chemistry of comets?

2.1. The missing link

Even if it can still be considered valid, the 'dirty snowball' model proposed by F. Whipple in 1950 (Whipple,

* Corresponding author. Fax: +33-1-45-17-15-64;
e-mail: cottin@lisa.univ-paris12.fr

1950), has long since evolved, and comets are now considered as the missing link between interstellar clouds and solar systems.

Indeed, nowadays, comets are represented as an aggregate of interstellar dust particles, which for some reason did not get incorporated into the planets during their formation. Held in the furthest and coldest regions of our solar system, they might have not been altered by thermal processes and thus should have kept the memory of the pristine composition of our natal interstellar cloud. But things are not as obvious as it seems at a first glance.

Dust particles are initially produced in the atmospheres of cool giant stars where they condense before being hurled into space by the radiation pressure. From infrared observations, it seems that these particles are mainly composed of silicates, as inferred by a strong absorption feature at $9.7\ \mu\text{m}$. Among others, a composition of an amorphous olivine such as MgSiFeO_4 seems to fit the astronomical observations (Greenberg and Li, 1996).

The cyclic evolutionary model proposed by Greenberg (1982) is then on its way: particles are transported back and forth between diffuse and molecular clouds from two to twenty times before the final molecular cloud collapses to form a solar nebula that leads to the formation of a solar system (Fig. 1). The density of diffuse clouds lies between 1 and $1000\ \text{atoms cm}^{-3}$, and consists mainly of H atoms at a temperature of over 100 K. The density of molecular clouds is over $1000\ \text{atoms per cm}^3$ and the temperature is around 10 K (Walmsley, 1994). Thus, the density is high enough to allow, by ion-molecule or grain surface reactions, the synthesis of light compounds such

as H_2 , H_2O , CO , CO_2 , NH_3 and CH_3OH . Since the temperature in molecular clouds is low, these molecules (except H_2) condense to form ices on the silicate grains. UV light from neighboring stars and galactic cosmic rays (GCR) then irradiate those ices. As it will be discussed later in this paper, laboratory irradiations of ices relevant to interstellar composition yield the production of a large variety of organic compounds. Indeed, UV photons and GCRs break the simple molecules and the resulting radicals may react with nearby molecules or be stored in ices. If ices are warmed up, more reactions are allowed by diffusion of the stored radicals.

The global evolution of clouds depends on dynamic processes on a galactic scale. They collide with each other, interact with stars, and on larger scales, are influenced by gravitational forces and by the revolution around the galactic center.

The optical properties of the interstellar medium suggest at least three populations of grains: (1) large grains (tenths of a micron) coated by a refractory organic mantle; (2) small carbonaceous particles ($< \text{hundredths}$ of a micron); (3) very small carbonaceous particles, probably large PAHs (Polycyclic Aromatic Hydrocarbons) (Li and Greenberg, 1997). A representation of particles from the first population is shown in Fig. 2. Small particles of the second and the third type may be trapped in ices surrounding the big ones.

When a dust particle is reinjected into the warmer diffuse medium, ices sublime, leaving only the silicate core embedded in the refractory mantle, which is partially eroded. Therefore, in a molecular cloud, there should be

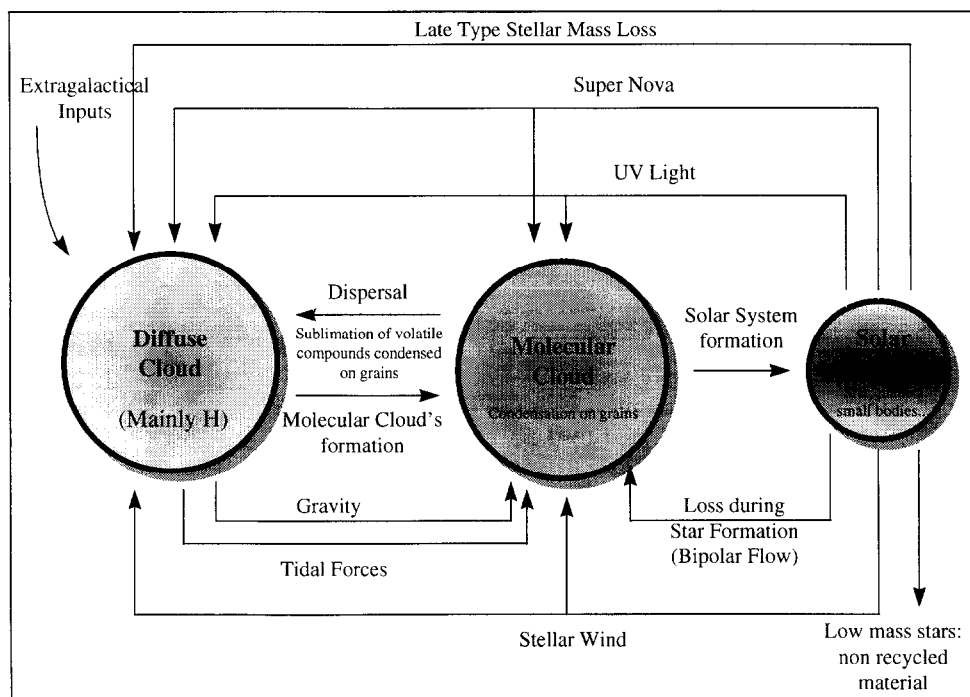


Fig. 1. Dynamic model of interstellar clouds. From W. Langer, Private Communication.

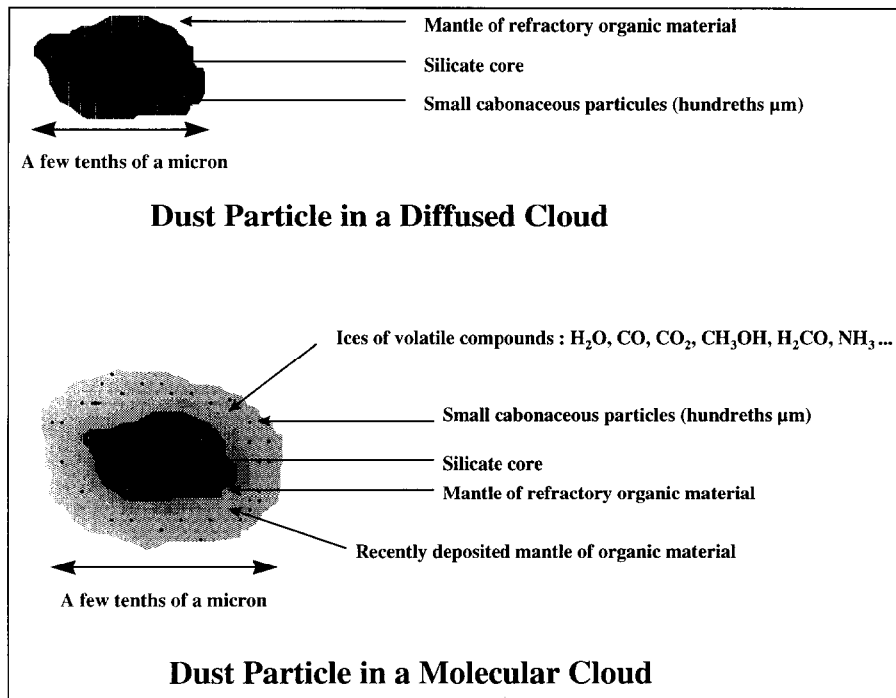


Fig. 2. Interstellar dust particle in diffuse and molecular clouds. From Greenberg's Model.

two layers of refractory mantle: the inner one which has been altered by the hard diffuse interstellar medium conditions, and the less processed outer layer, which has just formed in the molecular clouds. A complete cycle takes about 10^8 years, and the mean lifetime of a grain is about $5 \cdot 10^9$ years before being incorporated into a new solar system (Greenberg et al., 1995).

When a cloud finally reaches a critical mass, it collapses and grains are incorporated into the star and eventually the planets around it; thus material is reprocessed and the initial grain composition is lost. But some aggregates are held in safe regions of the solar system and should have kept their pristine composition: these are possibly the comets, dirty interstellar porous ($P \sim 0.8$) snowballs (Fig. 3).

But are comets really relevant to interstellar composition? Lunine et al. (1991) and Yamamoto (1985) have studied the conditions of comet formation and to what extent water and other volatiles of interstellar grains may have been volatilized. It appears that a significant fraction of interstellar grains have been altered out to a long distance from the protosun. Lunine et al. (1991) calculated that the quantity of water ice that sublimated when grains were falling into the solar nebula could reach 90% of the grain mass at 30 AU from the center of the nebula. This amount falls to less than 10% at 100 AU.

Another key point is that interstellar cloud chemistry (including radical and ion chemistry) leads, for organic compounds synthesized at low density and low temperature, to abundances different from those that would result from the solar nebula chemistry (neutral chemistry at

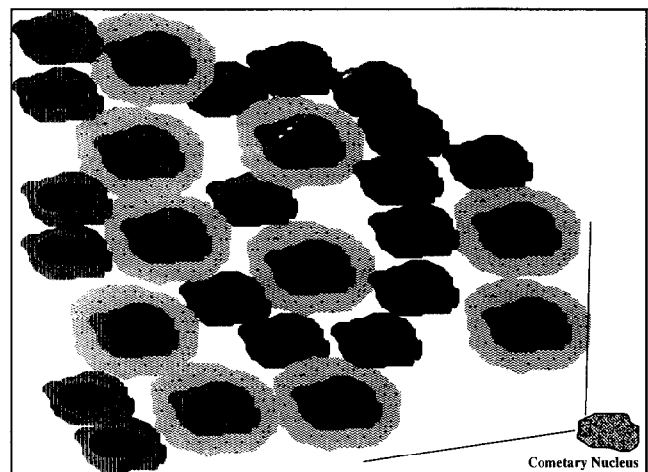


Fig. 3. From dust particles to a cometary nucleus.

warmer temperature and higher density). For instance, from the abundances of C_2H_2 (Brooke et al., 1996), C_2H_6 and CH_4 (Mumma et al., 1996) in comet Hyakutake, it seems that the cometary ices have been formed in our natal interstellar cloud.

There are other indicators of the origin of comets. Indeed, hydrogen in water exists in two spin states: ortho and para. According to the temperature at the moment of the formation of water, the ortho/para ratio differs. It has already been estimated for several comets: comet Halley (ortho/para = 2.5), comet Wilson (ortho/para = 3) (Crovisier, 1998 and ref therein), comet Hale-Bopp (ortho/para = 2.45) (Crovisier et al., 1997), and

comet P/Hartley 2 (ortho/para ~ 2.7) (Crovisier et al., 1998). Except for the comet Wilson, whose ortho/para ratio is found to be equal to the equilibrium value of 3, implying a formation temperature exceeding 60 K, other ratios suggest that water molecules were formed in interstellar clouds, at temperatures too low for the solar nebula: about 25–35 K. The D/H ratio in water is another interesting indicator we will talk about in the following section. It also leads to an interstellar origin of cometary ices, but they are probably mixed with ices reprocessed in the inner part of the solar nebula (Bockelée-Morvan et al., 1998; Meier et al., 1998).

Indeed, all observations do not lead to the conclusion that comets have kept an interstellar composition. We have seen earlier that the silicates in interstellar dust are thought to be in an amorphous state. The presence of a crystalline form of silicates in comets is an indication of warm processes (over 1300 K), which would significantly modify the original composition of interstellar grains: sublimation of volatiles and pyrolysis of the refractory mantle. Depending on the observed object, the cometary dust can contain amorphous and/or crystalline silicates (Crovisier, 1997; Hanner et al., 1994a,b). Recent observations of comet Hale–Bopp seem to indicate the presence of crystalline Mg-rich olivine (Mg_2SiO_4 : Forsterite which is a kind of silicate) (Crovisier et al., 1997; Hayward and Hanner, 1997) at a 20% level (Hanner, 1997). In the same comet at 7 AU from the Sun, water ice has been detected in an amorphous state (Davies et al., 1997), i.e. it has not encountered temperatures over 100 K since it condensed and thus may have kept the composition of interstellar grains. Lellouch et al. (1998) have detected crystalline ice in the grains of comet Hale–Bopp, but such a detection is not necessarily in contradiction to the previous one because the comet was closer to the Sun (2.9 AU) and hence warmer. Grains may have been reprocessed by higher temperatures in the coma. Moreover, if cometary ices are amorphous in the nucleus, this is coherent with numerical models, as we will see later in this paper. But how could we explain the fact that part of the silicates have experienced high temperatures?

One approach to this question is to consider that particles reprocessed at high temperature (i.e. crystalline) close to the forming sun could diffuse in a turbulent nebula out to the region of comets formation (see discussion in Bockelée-Morvan et al., 1998). It must also be considered that these crystalline silicates could also be ejected from the inner, warmer part of the nebula by the bipolar wind that results from the interaction of the accreting solar nebula and the magnetosphere of the young protosun. Some of them would reenter the solar system at great distances, where the temperature is much lower than in their ejection region, and be mixed with the surrounding amorphous dust particles (Shu et al., 1996). This could also explain that one finds materials in amorphous and crystalline states in comets.

A recent paper, Jewitt et al. (1997) concludes, from measurements of $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$ and $^{32}\text{S}/^{34}\text{S}$ ratios in comet Hale–Bopp, that cometary volatiles have their origin in the solar system and show no evidence of an interstellar composition. But the observed isotopic ratios (in the solar system) are only representative of the ratios of the protosolar cloud 4.6 Gyr ago. Interstellar ratios may have evolved since that time and be different from those observed in comets and the solar system. Thus the isotopic ratios of C, N and S in comets do not really rule out the interstellar origin of cometary material as it could seem at a first glance.

But are Hyakutake and Hale–Bopp typical comets?

Concerning our solar system, there seem to be two reservoirs of comets. First, the Kuiper Belt which extends from 30–100 AU from the Sun and could contain about 10^5 objects with a diameter larger than 100 km (Jewitt, 1999); most of the short period comets (period < 200 y) are believed to come from that region. Next, the Oort Cloud, which is spherical, spreads up to 10,000–100,000 AU and could contain from 10^{12} – 10^{13} objects (Weissman, 1996). The latter are thought to be comets formed between 5 and 30 AU from the Sun, which have been ejected to larger distances by gravitational interaction with the giant planets. Long period comets, including Hyakutake and Hale–Bopp, are thought to come from the Oort Cloud.

Therefore, comets accreted at 5 AU from the Sun and kept in the Oort Cloud, and those accreted beyond the orbit of Neptune in the Kuiper Belt, have been submitted to different thermal histories and thus should have different compositions. The only systematic study of cometary composition undertaken on 85 comets classed them into two categories of high and low C_2/CN ratios. The latter corresponds to Jupiter-family comets (A'Hearn et al., 1995). But observational data are insufficient to extend that study to other molecules such as parent compounds. Moreover, this study has been recently questioned by Schulz et al. (1998) who found that C_2/CN in comet P/Wirtanen could vary strongly and lead us to classify the comet in different families according to its heliocentric distance. Another study, based on the polarimetric properties of 22 comets, showed two classes of comets, with distinctly different dust properties (Levasseur-Regourd et al., 1996). But an explanation for such a difference is still missing, and it cannot be strictly related to the origin of the comets.

Moreover, as inferred by Farinella and Davis (1996) from theoretical modeling, short period comets could be fragmentation products of collisions of larger bodies in the Kuiper Belt. Such processes would certainly alter the composition of comets and may cast a doubt on their pristine nature.

Lunine writes in 1997 that, 'the gas and grain material would be progressively more similar to that of the molecular cloud as one moved outward beyond Jupiter and

Saturn. The most distant bodies of the solar system, Kuiper Belt objects and Oort Clouds comets might have retained an essentially interstellar composition'. Thus, comets are not the missing link, but more precisely many missing links, each corresponding to a different family of comets according to their origin and their thermal history before and after their accretion. A detailed study of one among them does not allow a final conclusion about the entire population, but would provide one piece of the puzzle that reconstructs the history of our solar system.

2.2. Do we drink interstellar water?

It is often stated that comets and meteorites have brought to Earth most of its water and organics. Planetesimals accreting at rather high temperature should not have kept their water, and protosolar water never condensed on the proto Earth. Thus either water rich solids were mixed with the protoplanetary material and outgassed later from the mantle, or they were introduced by surface impacts of comets or chondrites. As pointed out by Oro and Cosmovici in a recent review (Oro and Cosmovici, 1997), if the Moon is the result of a single giant collision between the Earth and a Mars-sized impactor as inferred by (Cameron and Benz, 1991) and more recently by (Ida et al., 1997), most of Earth's volatiles must have been vaporized and lost to space. Extra-terrestrial inputs become the most probable source of water on Earth.

In the same review, Oro and Cosmovici write that the D/H ratio measured in several comets is not far from the terrestrial value. But this is not exactly the case. The D/H ratio was measured in Halley (Balsiger et al., 1995; Eberhardt et al., 1995) and more recently, Hyakutake (Bockelée-Morvan et al., 1998), and Hale-Bopp (Meier et al., 1998). For these three comets, which are thought to have originated in the Oort Cloud, $D/H \sim 3 \times 10^{-4}$ in water, whereas D/H in water on Earth is 1.5×10^{-4} (Lecluse et al., 1996). If oceans had been imported by cometary impacts, we should find the same value within the range of uncertainties. Obviously, it is not the case. From these considerations, it is concluded that no more than 10% of water in the terrestrial oceans might have a cometary origin (Deloule et al., 1999; Robert, 1997).

The issue is still open. Other comets, originating from the Kuiper Belt for example, may have D/H ratios more compatible with terrestrial values, or rather than from comets, water could have been brought by carbonaceous meteorites whose D/H ratios are more suitable. For a detailed discussion about the D/H ratio in comets see Bockelée-Morvan et al. (1998).

2.3. Of ice and men

Early this century, Chamberlin and Chamberlin (1908) proposed that infalling carbonaceous chondrite meteor-

ites could have been an important source of terrestrial organic compounds. Oro was the first in 1961 to suggest that comets may have played a similar role, from observations of carbon- and nitrogen-containing radicals in cometary comae (Oro, 1961): 'I suggest that one of the important consequences of the interactions of comets with the Earth would be the accumulation on our planet of relatively large amounts of carbon compounds which are known to be transformed spontaneously into amino acids, purines and other biochemical compounds'.

It is now quite obvious that comets are important reservoirs of a wide variety of organic compounds:

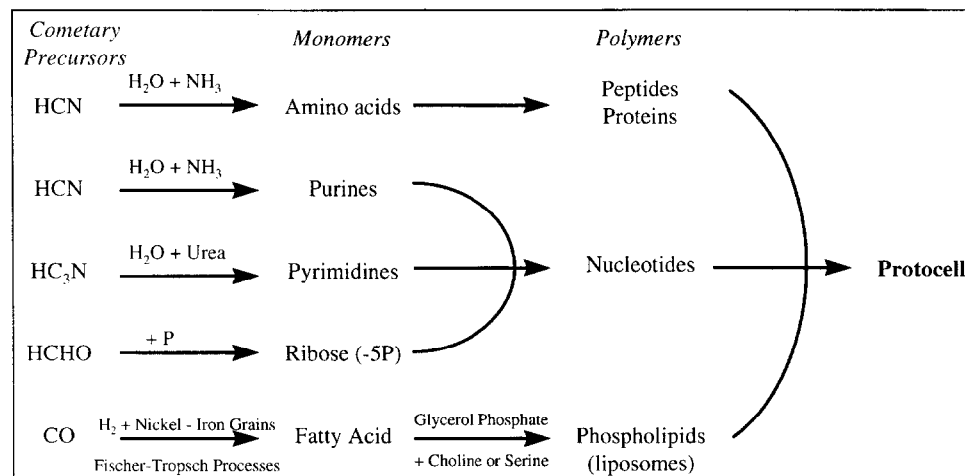
- From groundbased observations, which will be detailed in the next section of this paper, and lead to the detection of more than twenty stable small molecules;
- From in situ measurements by the Vega and Giotto Spacecrafts, which detected large molecules in dust grains by mass spectroscopy;
- From laboratory simulations of irradiated ices with composition relevant to the interstellar medium or to comets. They lead to the formation of a complex refractory organic mantle (this approach will make up one of the main parts of this paper).

Five families of compounds are considered to be the key prebiotic monomers required before starting a chemical evolution from which life would arise. These are amino-acids, purine bases (adenine and guanine), pyrimidines bases (cytosine, uracil and thymine), sugars and fatty acids. It is very interesting to note, that even if these compounds have not been detected in comets (maybe because of limitations in the sensitivity of telescopes, but also essentially because the synthesis of most of them requires liquid water), they can easily be produced in an early Earth environment from cometary precursors such as HCN, HC_3N , HCHO and CO which have been firmly detected in cometary comae (Table 1).

The other elements required, according to Table 1, for a protocell formation, are also present on comets. Phosphorus, which is involved in the synthesis of sugars, has been detected by mass spectroscopy ($m/e = 31$) in grains of comet Halley by the PUMA mass spectrometer on board Vega 1. But its abundance is very low and detection may have been affected by interference from ions such as CH_2OH^+ (Kissel and Krueger, 1987). However, analysis by laser probe mass spectroscopy of interplanetary dust particles (IDPs), whose cometary origin is probable, has led to the detection of PO_2 and PO_3 anions (Radicati-Di-Brozolo et al., 1986). Ni and Fe have been detected in comet Ikeya-Seki and Halley (see Crovisier, 1997 for a recent review).

Nevertheless, complex compounds of exobiological interest may also be present in comets. The only detection of adenine is a very tentative interpretation of PUMA's mass spectra of comet Halley's dust (Kissel and Krueger, 1987). Such a molecule could be synthesized by HCN

Table 1
Prebiotic syntheses from cometary molecules



From Oro and Cosmovici, 1997—courtesy of C.B. Cosmovici.

condensation without any liquid water (Oro and Cosmovici, 1997; Wakamatsu et al., 1966). Moreover, as we will see later in this paper, when ices relevant to the composition of interplanetary dust particles or comets are irradiated, complex molecules are formed, and among them, the simplest amino acid, glycine (Briggs et al., 1992). After an acid hydrolysis in water other amino-acids, such as alanine, have also been identified (Kobayashi et al., 1995).

Thus, comets may have imported prebiotic elements to early Earth, which, when mixed with liquid water, have allowed the synthesis of all molecules thought to be necessary for the origin of life. But before seeding the oceans, those compounds have to survive pyrolysis while the comet is slowed down and warmed up by the Earth's atmosphere, and the ensuing impact.

This aspect of the question has been treated by (Chyba et al., 1990). It appears that organic compounds (even amino acids, if present) contained in cometary impactors of 100–200 m in size could survive a collision with Earth in a 10 bar CO₂ atmosphere thanks to an efficient aerobreaking. Comparisons with Venus and Mars lead us to think that it is the most probable composition of the primitive atmosphere. The authors note in their conclusion that 'It is intriguing that it is exactly these dense CO₂ atmospheres, where photochemical production of organic molecules should be the most difficult, in which intact cometary organics would be delivered in large amounts'. Indeed, organic syntheses are efficient in reduced atmospheres, even weakly reduced atmospheres such as that of Titan (N₂, CH₄), whereas they are very difficult in the highly oxidized environment that must have been the early Earth's atmosphere.

3. Observations

There is no direct indication of the composition of the cometary nucleus. The only data are spectroscopic observations of the comae and in-situ analysis of gas and grains, mainly by Giotto, Vega-1 and -2 Spacecrafts, during the 1986 Halley flyby. Estimations concerning the chemical composition of a comet nucleus have been made by Greenberg (1998) from observations and laboratory simulations: 26% of a comet consists of silicates, 23% of a refractory organic mantle and 9% are attogram particles. The 42% remaining consists of a mixture of volatile compounds dominated by water (around 80% by number).

In most cases, water is indirectly detected from its photodecomposition products (OH, O, H), but water can also be directly detected in the coma of some comets (see for example for comet Wilson: Larson et al., 1989 and for comet Hale-Bopp: Crovisier et al., 1997 and Dello Russo et al., 1998). As for water ice, it is very difficult to observe because either it is hidden by the surrounding coma, or the comet is too far away and hence too faint to be observed. Nevertheless, it has recently been detected for the first time in icy grains of comet Hale-Bopp (Davies et al., 1997; Lellouch et al., 1998).

Observations give the number of molecules ejected from the nucleus per second, Q_g . For typical comets $Q_{\text{H}_2\text{O}} = 10^{27} - 10^{30}$ (Crifo, 1994). The abundance of any other molecule is usually given relative to water for a heliocentric distance of 1 AU.

Abundances of molecules detected in the gaseous phase and some additional upper limits are given in Table 2. For recent reviews and discussions about observational constraints and uncertainties see Bockelée-Morvan

(1997) and Crovisier (1997), but it must be noted that relative abundances are spoilt by uncertainties because observations of water and the molecule are rarely simultaneous and cometary activity can vary from one observation to the other. Moreover some molecules are not directly emitted from the nucleus but from extended sources: dust particles or decomposition of higher molecular weight molecules. This is the case for CO and H₂CO, which could be decomposition products of the formaldehyde polymer, polyoxymethylene (—CH₂—O—)_n, POM (see for instance: Boice et al., 1990; DiSanti et al., 1997; Greenberg and Li, 1998; Meier et al., 1993). Carbon suboxide C₃O₂ is also evoked as an explanation for the extended source of CO (Huntress et al., 1991); it has not yet been detected in comets but, as we will see later in this paper, has been observed in experimental simulations (Brucato et al., 1997a; Moore et al., 1991). It must also be pointed out that the presence of phenanthrene is proposed by Moreels et al. (1994) and other PAHs are also inferred from a feature at 3.28 μ m in several comets (Bockelée-Morvan et al., 1995).

The Giotto-PICCA instrument, devoted to gas phase analysis of organic compounds, and the Vega-PUMA instrument, devoted to dust composition analysis, have detected in the coma of comet Halley heavier compounds than those firmly detected by remote sensing. The most fruitful works have been performed by Kissel and Krueger (Kissel and Krueger, 1987; Krueger and Kissel, 1987). To interpret the PUMA's mass spectra, they consider that all sudden dissipation processes near solid surfaces after an impact are governed by the same rules of molecular ion formation. Such impacts occur when a dust particle hits the mass spectrometer's target. This hypothesis yields a good agreement between their predictions and other observations for small molecules (e.g. HCN, CH₃CN). For larger molecules the problem is more complex as they cannot survive the transfer of velocity momentum in the impact process. Thus their identification of purines and adenine, for example, is very tentative.

First interpretations of the heavy-ion mass spectra from the PICCA instrument led Huebner (1987) to conclude the presence of polyoxymethylene in comet Halley. After further analyses Huebner et al. (1989) confirmed that detection and discussed the presence of POM derivatives such as sulfur copolymers. The presence of POM in comets is coherent with the detection of extended sources of CO and H₂CO in the coma. Indeed, these molecules

could be photodecomposition products of POM. The authors also suggest the presence of HCN polymers such as polyaminocyanomethylene (PACM: (NH₂—C—CN)_n), even if these polymers should be very difficult to detect because in the coma HCN/H₂CO \sim 0.1 (Huebner et al., 1989). Moreover HCN polymers should be more difficult to detect than H₂CO's ones: Krueger et al. (1991) have calculated from thermodynamic considerations that N containing polymers should be less volatile than O containing polymers. The presence of HCN/H₂CO copolymers could also be suggested on comets because these two molecules polymerize very easily by themselves.

In a more recent paper Mitchell et al. (1992) show that the mass spectrum pattern which leads Huebner to announce the detection of polyoxymethylene, is only characteristic of a mixing of molecules composed of C, H, O and N atoms (CHON molecules). Therefore, PICCA mass spectra do not imply the presence of POM, but only of a large diversity of CHON molecules, among which POM could be present. The most we can say, if we consider laboratory simulation results, is that the presence of POM on cometary nuclei is possible.

Compounds detected in comet Halley by mass spectroscopy are reported in Table 3.

4. Numerical simulations

This section is not an exhaustive review of numerical models, but a general overview of the topic. We note especially that physical modeling is more extensive than it appears in this paper. We will only quote four examples to illustrate the variety of numerical studies of comets and to point out their role in the study of cometary chemistry.

There are two main kinds of numerical models concerning comets: those dealing with physics and those dealing with chemistry. In both cases it is a question of simulating the behavior of either the nucleus or the coma behavior. The four aspects are obviously interdependent if one wants, for example, to estimate nuclei composition from observations of comae; the chemistry of the coma cannot be simulated without a good description of emission and transport processes, but such a module is so complex and uncertain that the chemical scheme must remain fairly simple. Thus, to date, they have been treated separately.

Model	Physical	Chemical
Nucleus	(Enzian, 1997; Enzian et al., 1997)	(Navarro-Gonzalez et al., 1992; Navarro-Gonzalez and Romero, 1996)
Coma	(Crifo et al., 1995; Crifo and Rodionov, 1997a,b)	(Huebner et al., 1991; Schmidt et al., 1988; Wegmann et al., 1987)

Table 2

Molecular abundances of gaseous compounds in comets. From Crovisier, 1994, and updated by us for recent observations. References are as exhaustive as possible to indicate all initial sources

Compound	Abundance	Comet	Method	Reference
H ₂ O	100	Many	Photod, products	
		P/H, Wilson	IR	1–5
		P/H	NMS	6
		Hale–Bopp	OH (UV)	70
			OH (radio)	71, 72
CO	2–20	Several	UV	7–9
		P/H, Austin	IR	2, 10
		P/H	NMS	11
	2–8.5	Brad., P/H, Aust., Levy	UV	52
	<1	P/Hartley 2	UV	12
	5	Hyakutake	IR	48
	30–43		Radio	65, 74
CO ₂	20	Hale–Bopp	Radio, IR, UV	77
	2.7	P/H	IR	2
	3.5	P/H	NMS	6
	4–7	P/Hartley 2, Bradfield, P/H, Austin	CO Cameron band	12, 52
	2.2–3.6	S/L	CO Cameron band	52
	7–13	Levy	CO Cameron band	52
	4	Hyakutake	CO Cameron band	76
	6	Hale–Bopp	IR	77
H ₂ CO	0.03–1.5	Several	Radio	13–16
	<1	Several	IR	17
	4	P/H	IR	2
	>3.8	P/H	NMS, IMS	18–20
	0.2–1	Hyakutake	Radio	54, 65, 74
	~1	Hale–Bopp	Radio	77
CH ₃ OH	1–7	Several	Radio	16, 21–24
		P/H	IR	25, 26
			NMS, IMS	19, 27, 53
	0.9–2	Hyakutake	Radio	54, 56, 65, 74
	2	Hale–Bopp	Radio, IR	77
C ₂ H ₅ OH	<0.5	Levy	Radio	28
HCOOH	<0.2	Austin, Levy	Radio	28
	0.05	Hale–Bopp	Radio	60, 77
HCOOCH ₃	0.05	Hale–Bopp	Radio	63, 77
CH ₄	<0.5–2	P/H, Wilson, Levy	IR	5, 29, 30, 31
	2	P/H	IMS	32
	0.7	Hyakutake	IR	48
	~1	Hale–Bopp	IR	77
C ₂ H ₆	0.4	Hyakutake	IR	48
	~0.5	Hale–Bopp	IR	77
C ₂ H ₂	0.3–0.9	Hyakutake	IR	50
	0.2	Hale–Bopp	IR	58
Phenanthrene	0.15	Halley	UV	73
NH ₃	0.1–0.4	Several	NH, NH ₂ (vis)	33, 34
	0.4–1	P/H	NH (UV)	35
	0.5–2	P/H	IMS, NMS	32, 36
	0.55	P/H	NH ₂ (vis)	51
	0.3	Hyakutake	Radio	69
	1.4	Hale–Bopp	Radio	67
HCN	0.05–0.2	Several	Radio	15, 23, 24, 37, 38
	0.02	P/H	NMS, IMS	36
	0.1–0.2	Hyakutake	Radio	49, 65, 74
	0.2	Hale–Bopp	IR	58
HNC	0.007	Hyakutake	Radio	74
	<0.004 (nucleus)	Hale–Bopp	Radio	79
HNCO	0.07	Hyakutake	Radio	74
	0.04–0.13	Hale–Bopp	Radio	75
CH ₃ CN	0.02	Hyakutake	Radio	54, 55
	0.02	Hale–Bopp	Radio	59, 77

Continued on next page

Table 2
Continued

Compound	Abundance	Comet	Method	Reference
HC ₃ N	<0.02	P/H, Levy	Radio	28, 37
	0.019	Hale-Bopp	Radio	75
N ₂	0.02–0.2	P/H, Bradfield	N ₂ ⁺ (vis)	39, 40
	<1.5	P/H	NMS, IMS	11, 19
NH ₂ CHO	0.01–0.08	Hale-Bopp	Radio	62, 75
H ₂ S	0.1–0.3	Austin, Levy, P/S-T	Radio	21, 22, 24, 41
	0.4–0.5	P/H	IMS, NMS	19, 42, 53
	0.3–0.6	Hyakutake	Radio	54, 56
	1.6	Hale-Bopp	Radio	77
H ₂ CS	<0.1	Levy	Radio	28
	0.02	Hale-Bopp	Radio	64, 77
CS ₂	0.1	Several	CS (UV)	9
	0.2	Hale-Bopp	CS (UV, radio)	77
S ₂	0.05	IRAS-A-A	UV	43, 44
	0.005	Hyakutake	UV	54, 57
OCS	<0.3	Levy	Radio	41
	<0.5	P/H, Austin	IR	2, 45
	0.1	Hyakutake	Radio	56
	0.6	Hale-Bopp	Radio	64, 75
SO ₂	<0.001	P/H, Bradfield	UV	46
	0.15	Hale-Bopp	Radio	61, 77, 78
SO	0.2–0.8	Hale-Bopp	Radio	75
He	<3	Austin	UV	47
Ar	<17	Austin, Levy	UV	8, 47
Ne	<0.6	Hale-Bopp	UV	66

1 (Mumma et al., 1986); 2 (Combes et al., 1988); 3 (Krasnopolsky et al., 1986); 4 (Weaver et al., 1994); 5 (Larson et al., 1989); 6 (Krankowsky et al., 1986); 7 (Feldman and Brune, 1976); 8 (Feldman et al., 1991); 9 (Feldman, 1991) and refs therein; 10 (DiSanti et al., 1992b); 11 (Eberhardt et al., 1987); 12 (Weaver et al., 1994); 13 (Snyder et al., 1989); 14 (Colom et al., 1992); 15 (Schloerb and Ge, 1992); 16 (Bockelée-Morvan et al., 1994); 17 (Reuter et al., 1992); 18 (Krankowsky, 1991); 19 (Geiss et al., 1991); 20 (Meier et al., 1993); 21 (Bockelée-Morvan et al., 1990); 22 (Bockelée-Morvan et al., 1991); 23 (Bockelée-Morvan et al., 1993); 24 (Despois et al., 1996); 25 (Hoban et al., 1991); 26 (Hoban et al., 1993); 27 (Eberhardt et al., 1991); 28 (Crovisier et al., 1993); 29 (Dratz et al., 1987); 30 (Kawara et al., 1988); 31 (Brooke et al., 1991); 32 (Allen et al., 1987); 33 (Magee-Sauer et al., 1989); 34 (Wyckoff et al., 1991a); 35 (Feldman et al., 1993); 36 (Ip et al., 1990); 37 (Crovisier and Schloerb, 1991) and refs therein; 38 (Wootten et al., 1994); 39 (Wyckoff et al., 1991b); 40 (Lutz et al., 1993); 41 (Crovisier et al., 1991); 42 (Marconi et al., 1990); 43 (A'Hearn et al., 1983); 44 (Budzien and Feldman, 1992); 45 (DiSanti et al., 1992a); 46 (Kim and A'Hearn, 1991); 47 (Stern et al., 1992); 48 (Mumma et al., 1996); 49 (Irvine et al., 1996); 50 (Brooke et al., 1996); 51 (Smythe et al., 1995); 52 (Feldman et al., 1997); 53 (Eberhardt et al., 1994); 54 (Bockelée-Morvan, 1997); 55 (Dutrey et al., 1996); 56 (Woodney et al., 1997); 57 (Weaver et al., 1996); 58 (Brooke et al., 1997); 59 (Biver et al., 1997); 60 (Wink et al., 1997b); 61 (Wink et al., 1997a); 62 (Mehring et al., 1997); 63 (Colom et al., 1997); 64 (Woodney et al., 1997); 65 (Womack et al., 1997); 66 (Krasnopolsky et al., 1997); 67 (Bird et al., 1997); 68 (Crovisier, 1997); 69 (Palmer et al., 1996); 70 (Weaver et al., 1997); 71 (Biver et al., 1997); 72 (Crovisier et al., 1997); 73 (Moreels et al., 1994); 74 (Lis et al., 1997); 75 (Lis et al., 1998); 76 (McPhate et al., 1996); 77 (Crovisier, 1998); 78 (Bockelée-Morvan et al., 1997); 79 (Irvine et al., 1998).

One of the most recent physical models of the nucleus has been developed by Enzian (Enzian, 1997; Enzian et al., 1997). Crystallization of amorphous water ice during which trapped gases are released (mainly CO), diffusion of gas and heat, sublimation and recondensation are taken into account inside the nucleus. This model can explain the erratic behavior of comet 29P/Schwassmann-Wachmann 1 from a coupling of the crystallization of water ice and diffusion processes. Moreover, the latent heat released during crystallization is sufficient to explain the activity of comet Hale-Bopp at large heliocentric distances. The advantage of such a work is that one can compare simulations to observations for different initial compositions of the nucleus. The best fit is provided in the case of a nucleus composed of amorphous ice and

is coherent with the hypothesis that water ice is in an amorphous state in cometary nuclei and thus may have kept an interstellar composition.

Concerning the chemistry of the nucleus, models are less complex because of the lack of experimental data about the chemical mechanisms and rate constants of reactions involving cometary compounds in the solid state. This is the case with the model presented in Navarro-Gonzalez et al. (1992) and Navarro-Gonzalez and Romero (1996). These papers present the effect of ionizing radiation (cosmic rays and embedded radionuclides) on the cometary material: pristine organic compounds should not be altered except in the external layers of the comet. It is also predicted that an original enantiomeric excess of alanine would not be destroyed by radior-

Table 3

Organic molecules inferred from mass spectra of gas and dust particles in comet Halley

Molecule	Family	Mass spectrometer	Confidence level	Reference
Hydrocyanic acid	C-N-H	PUMA, PICCA	Confirmed	1, 2, 3
Acetonitrile	C-N-H	PUMA, PICCA	Confirmed	1, 2, 3
Formaldehyde	C-O-H	PUMA, PICCA	Confirmed	3
Formic acid	C-O-H	PUMA	Confirmed	1, 2
Ammonia	N-H	PUMA	Confirmed	2
Acetaldehyde	C-O-H	PUMA, PICCA	High	1, 3
Acetic acid	C-O-H	PUMA	High	1
Polyoxymethylene	C-O-H	PICCA	High (itself or derivatives)	4, 5
Iminoethane	C-N-H	PUMA	Medium	1, 2
Aminoethane	C-N-H	PUMA	Medium	1, 2
Pyrroline	C-N-H	PUMA	Medium	1
Pyrrole	C-N-H	PUMA	Medium	1, 2
Imidazole	C-N-H	PUMA	Medium	1
Pyridine	C-N-H	PUMA	Medium	1, 2
Pyrimidine	C-N-H	PUMA	Medium	1, 2
Cyclopropenyl	C-H	PICCA	Medium	3, 6
Pentyne	C-H	PUMA	Low	1
Hexyne	C-H	PUMA	Low	1
Butadiene	C-H	PUMA	Low	1
Pentadiene	C-H	PUMA	Low	1
Cyclopentene	C-H	PUMA	Low	1
Cyclopentadiene	C-H	PUMA	Low	1
Cyclohexene	C-H	PUMA	Low	1
Cyclohexadiene	C-H	PUMA	Low	1
Benzene	C-H	PUMA	Low	1
Toluene	C-H	PUMA	Low	1
Propanenitrile	C-N-H	PUMA	Low	1
Iminomethane	C-N-H	PUMA	Low	1
Iminopropene	C-N-H	PUMA	Low	1
Purine	C-N-H	PUMA	Low	1, 2
Adenine	C-N-H	PUMA	Low	1, 2
Polyaminocyanomethylene	C-N-H	PICCA	Low	5
Cyanic acid	C-N-O-H	PUMA	Low	1, 2
Methanolitrile	C-N-O-H	PUMA	Low	1
Methanalimine	C-N-O-H	PUMA	Low	1
Aminomethanol	C-N-O-H	PUMA	Low	2
Aminomethanal	C-N-O-H	PUMA	Low	2
Oxyimidazole	C-N-O-H	PUMA	Low	1
Oxypyrimidine	C-N-O-H	PUMA	Low	1
Xanthine	C-N-O-H	PUMA	Low	1

1 (Kissel and Krueger, 1987); 2 (Krueger and Kissel, 1987); 3 (Krueger et al., 1991); 4 (Huebner, 1987); 5 (Huebner et al., 1989); 6 (Korth et al., 1989).

The confidence levels of detections by MS are established as follows: Confirmed: molecule also detected by remote observations; High: molecule not detected by remote observations but present after laboratory irradiations of cometary ice analogs; Medium: molecule detected only by mass spectroscopy with a good confidence level according to the authors; Low: molecule only inferred by mass spectroscopy with a low confidence level according to the authors.

acemisation during the decay of radionuclides. At the very most it should be attenuated, but comets could have contributed to the origin of chirality on Earth. The limitation of this work is that the kinetic data used in the calculations are for the liquid phase, which may be very far from reality. Therefore the results must be considered with caution.

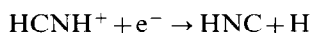
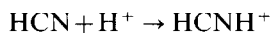
The coma is also very complex to simulate. The work developed in Crifo et al. (1995); Crifo and Rodionov (1997a,b) is a progression towards a 3-D model of a circumnuclear coma according to the properties of the

nuclei and dust. This complex physical model gives the gas density and velocity for the first tens of kilometers from the nucleus. It appears that the brightness patterns of the near nucleus dust coma are not direct tracers of the nucleus activity as thought before; the relationship between the coma structure and the dust and gas production geometry is not simple. This work strengthens the idea that without a good comprehension of all processes, misinterpretations can spring from artifacts. By extension it must be noted that it is all the more true for the chemistry: the appearance or disappearance of compounds can

be the consequence of either transport or photochemistry, and only complex numerical models will allow the resolution of such questions.

The most advanced work concerning the chemistry of the coma is the magneto-hydrodynamic model described in Huebner et al. (1991); Schmidt et al. (1988) and Wegmann et al. (1987). The physico-chemical interactions of the coma with the solar wind are taken into account. Parent molecules leaving the nucleus are transformed into very reactive ions and radicals by solar UV radiation and the resulting gas phase reactions. In Wegmann et al. (1987), the authors calculate the ion density profile for comet Halley along the Giotto trajectory. The model is in rather good agreement with MS observations for light ions (up to 21 AMU), but it becomes less accurate for heavier ions and for calculations made at large distances from the nucleus. The chemistry of heavy molecules is far from being well documented and experimental data for photodecomposition in the far UV of most inferred cometary compounds of high molecular mass, such as those presented in Table 3, are missing.

The importance of such chemical models has been recently emphasized by Irvine et al. (1998) and Rodgers and Charnley (1998). They have shown using recent models that HNC in comet Hale–Bopp was not directly emitted from the nucleus, but produced from HCN chemistry in the coma, (Irvine et al., 1998):



When HNC was first detected in comet Hyakutake, its abundance was interpreted as evidence for the interstellar origin of cometary ices (Irvine et al., 1996). Now, it is clear that it is not as obvious as it seemed. Moreover, production processes can vary from one comet to another, because in contrast to Hale–Bopp, in comet Hyakutake, HNC can either be produced from the nucleus or by photodestruction of a parent molecule (Rodgers and Charnley, 1998). But we have to keep in mind that these discrepancies could also be due to the limitations of the models.

We are still very far from modeling all cometary process well. As written in Huebner et al. (1991): ‘In a comprehensive, global model, the physics and chemistry of nucleus surface layer, the gas production, the dust entrainment, the dissociation and ionization of the coma gas, the radiation pressure on the dust and gas species, the solar wind interaction with the coma ions and with the coma neutrals through charge exchange and momentum exchange by elastic collisions, and the plasma and dust tail formation (to mention just a few important processes) are closely interwoven. There is little hope that the global model will ever be able to encompass all of these processes. Restricted global models are a natural consequence of the complexity.’

5. Experimental simulations

The third way to improve our knowledge of the composition of comets is by performing experimental simulations. The principle of such experiments is the following: from observations of the most abundant species in comae and in the interstellar medium, one can infer the probable composition of nuclei. A gaseous sample of the key species is deposited under vacuum on a cold substrate and irradiated during or after deposition by UV photons or charged particles. Condensed ices are sometimes simply warmed up slowly without irradiation. When the sample is warmed up for analysis a refractory organic residue remains on the substrate as the volatiles sublimate. Mayo Greenberg has called this residue Yellow Stuff. Bernstein et al. (1997) have shown that the organic residue is formed only when the initial mixture of ices contains polar molecules such as CH_3OH and NH_3 .

Historically, from the end of the seventies, these experiments were performed to study the composition of interstellar dust particles, but they are obviously linked to comets since the latter are considered as dust aggregates.

The diversity of organic compounds synthesized is remarkable but their identification is seldom exhaustive. Most of the experiments carried out on cometary analogs are summed up in Appendix A. Table 4 is a simplified list of all the detected compounds. The simplest compounds such as CO , CO_2 , H_2CO and CH_4 are detected in almost all the experiments, if the irradiated ice contains the appropriate elements. For more complex molecules, it depends on the ice composition and the nature of the energy source.

In addition to chemical transformations, it must be mentioned that experiments on the trapping of gases during ice condensation suggest that these processes play an important role in determining the composition of the ice and could lead to important enrichment or depletion between the gaseous and solid phases (Notesco and Barnun, 1996, 1997; Notesco et al., 1997). But in this section, we will focus on experimental simulations that lead to modifications of ice composition after an energy deposition, pointing out some of the molecules of cometary interest synthesized.

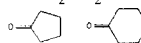
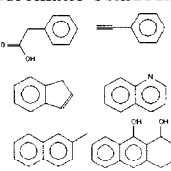
5.1. Energy deposition

Three kinds of energy deposition simulate processes occurring during the dust or comet’s lifetime, in the interstellar clouds or in the solar system.

In interstellar clouds, dust particles are subjected to irradiation by:

- Charged particles: galactic cosmic rays.
- UV: direct from neighboring stars in the outer regions

Table 4
Molecules detected after experimental simulations on cometary analogs

Hydrocarbons : CH_4 C_2H_2 , C_2H_4 , C_2H_6 C_3H_8 , C_4H_{10} C_5H_{10} , C_5H_{12} C_6H_{12} , C_6H_{14} C_7H_{16}	Ketones : CH_3COCH_3 $HOCH_2COCH_3$ $HOCH_2CH_2COCH_3$ 	Alcohols : CH_3OH CH_3CH_2OH $HOCH_2CH_2OH$ $HOCH_2CH(OH)CH_2OH$ $C_4H_8(OH)_2$ C_5H_8OH (t) $C_5H_{11}OH$
Amides : NH_2CHO CH_3CONH_2 $HOCH_2CONH_2$ $NH_2(CO)_2NH_2$ $HOCH_2CH(OH)CONH_2$	Carboxylic Acids : $HCOOH$ CH_3COOH (t) $HOCH_2COOH$ $HOCH_2CH(OH)COOH$ $HOCH_2CH_2COOH$ $NH_2COCOOH$	Amino Acids : NH_2CH_2COOH (Glycine) $NH_2CH(CH_3)COOH$ (Alanine) $CH_3CH_2CH(NH_2)COOH$ (α ABA) $CH_3CH(NH_2)CH_2COOH$ (β ABA) $(CH_2NH_2)(CH_3)CHCOOH$ (AIBA)
Amines : $HOCH_2CH_2NH_2$ $HCNH(NH_2)$	Aromatic Compounds : 	Esters : $HCOOCH_3$ CH_3COOCH_3 $CH_3CH_2COOCH_3$
Aldehydes : H_2CO CH_3OCH_2CHO (t)	Others : CO , CO_2 , C_3O_2 , H_2O_2 , H_2CO_3 , N_2H_4 $HNCO$, NH_2CONH_2 , $NH_2CONHCONH_2$ $(CH_2)_6N_4$: HMT, $(-CH_2-O-)_n$: POM	Ethers : $CH_3OCH_2OCH_3$ (t) $C_3H_6O_3$ (Trioxane) (t)

Italic letters refer to molecules detected in comets. (t) means tentative detection only in the analogs. For more details see text and Appendix A.

or induced by galactic cosmic rays for the inner regions of dense clouds.

- Thermal processes: cycle between cold dense clouds and warmer diffuse medium.

In the solar system, comets are undergoing the same processes:

- Charged particles: galactic cosmic rays, mainly in the Kuiper Belt and the Oort Cloud.
- UV: mainly in the inner solar system when the comet is close to the Sun.
- Thermal processes: during the formation of the solar system (depending on the region in which the comet accretes), and in the inner solar system (if the comet gets close to the Sun on its orbit).

Except during the accretion phase, these last three processes in the solar system affect only the outer layers of the comet.

Differences between the products according to the energy sources could give information on the history of comets, but as we will see, it is rather the analytical method (IR: infrared spectroscopy, HPLC: high performance liquid chromatography, GC-MS: gas chromatography coupled with mass spectroscopy, MS: mass spectroscopy) than the energy deposited which determines the molecules detected.

5.2. UV irradiation

The two main UV irradiation experiments of ice analogs are at Leiden-Netherlands (Greenberg's team) and at AMES-USA (Allamandola and Sandford's team). These two experimental setups are analogous and were first devoted to the study of interstellar ices (Fig. 4a and b). UV irradiation is performed using a flowing hydrogen discharge lamp (powered by a microwave cavity) delivering mainly Lyman α photons (122 nm) and a broad band of photons centered at 160 nm (see Allamandola et al., 1988 for a detailed description).

During these experiments a wide variety of organic compounds have been identified. From an initial mix of $H_2O:CO:NH_3$ (ratio = 5:5:1), glycine, the simplest amino acid, acetamide, glyceramide, and many other molecules have been detected by GC-MS (Briggs et al., 1992). Analysis by MS-MS on the organic residues formed, leads to the detection of heavier compounds: several cyclic molecules and PAHs (Greenberg and Mendoza-Gomez, 1993). This has to be related to the detection of phenanthrene in comet Halley (Moreels et al., 1994). It seems as though the nature of the molecules detected depends on the analytical method employed. The composition of the heaviest part of the residue is still unknown but an elemental composition based on the overall structure of the mass spectra is given by Greenberg and Li (1998) (C:O:N:H = 1:0.06: > 0.001:1.1).

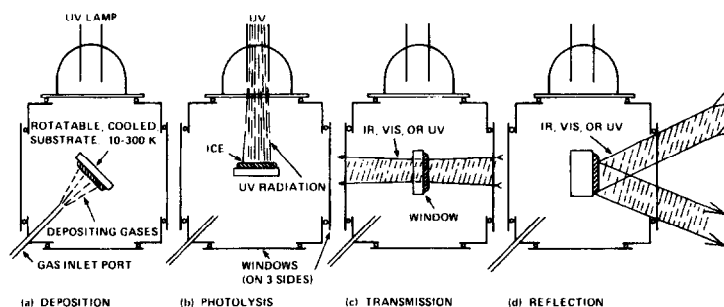


Fig. 4a. Schematic representation of a UV irradiation sample chamber. Different experimental configurations are shown. (From Allamandola et al., 1988 – Courtesy of L. Allamandola)

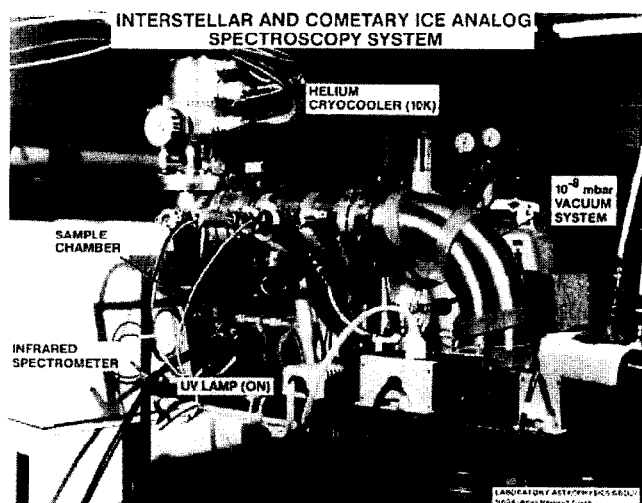


Fig. 4b. Picture of the AMES experimental system. (Courtesy of M. P. Bernstein, also available on <http://web99.arc.nasa.gov/~astrochml>)

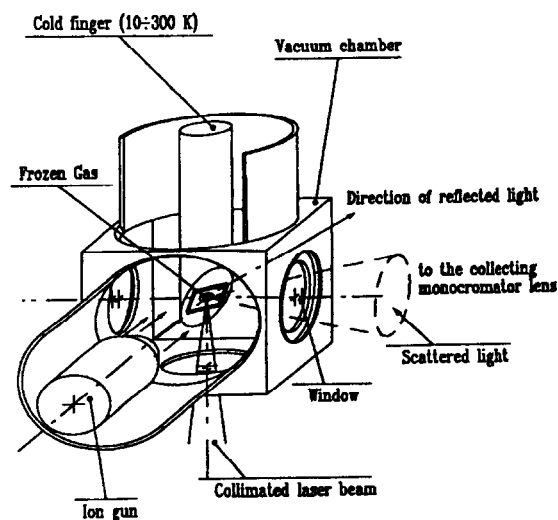


Fig. 4c. Schematic view of the experimental apparatus used to obtain Raman spectra of ion-irradiated ices. (From Strazzulla et al., 1991 – Courtesy of G. Strazzulla)

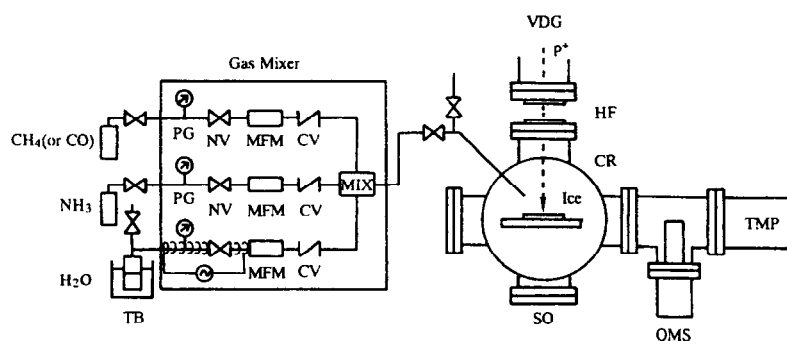


Fig. 4d. Experimental setup used to obtain amino-acids in proton irradiated ices. (From Kobayashi et al., 1995 – Courtesy of K. Kobayashi)

Fig. 4. Some experimental setups which have provided the main results concerning irradiation of analogs of cometary ices.

Among the molecules synthesized after such irradiations of ices, one of them is of great interest. Bernstein et al. (1995) have identified abundant hexamethylenetetramine (HMT— $C_6H_{12}N_4$) in the refractory mantle. Its detection has been performed by IR, GC-MS, and ^{13}C NMR. This compound has exobiological implications since its acid hydrolysis products are amino-acids (Wolman et al., 1971). Typically, for an initial composition of $H_2O:CH_3OH:CO:NH_3$ (10:5:1:1), the

organic residue at 300 K contains HMT (~60%), ethers and POM-like polymers (~20%), ketones and amides (~20%). One-fifth of the carbon and 1/2 of the nitrogen from the initial ice composition remain in the refractory part (Bernstein et al., 1995). Thus a large fraction of HMT is formed (60% of the residue) whereas only 5% NH_3 is present in the ice before irradiation. According to Bernstein et al. (1995), this could explain why the detection of frozen ammonia in interstellar ice is so difficult,

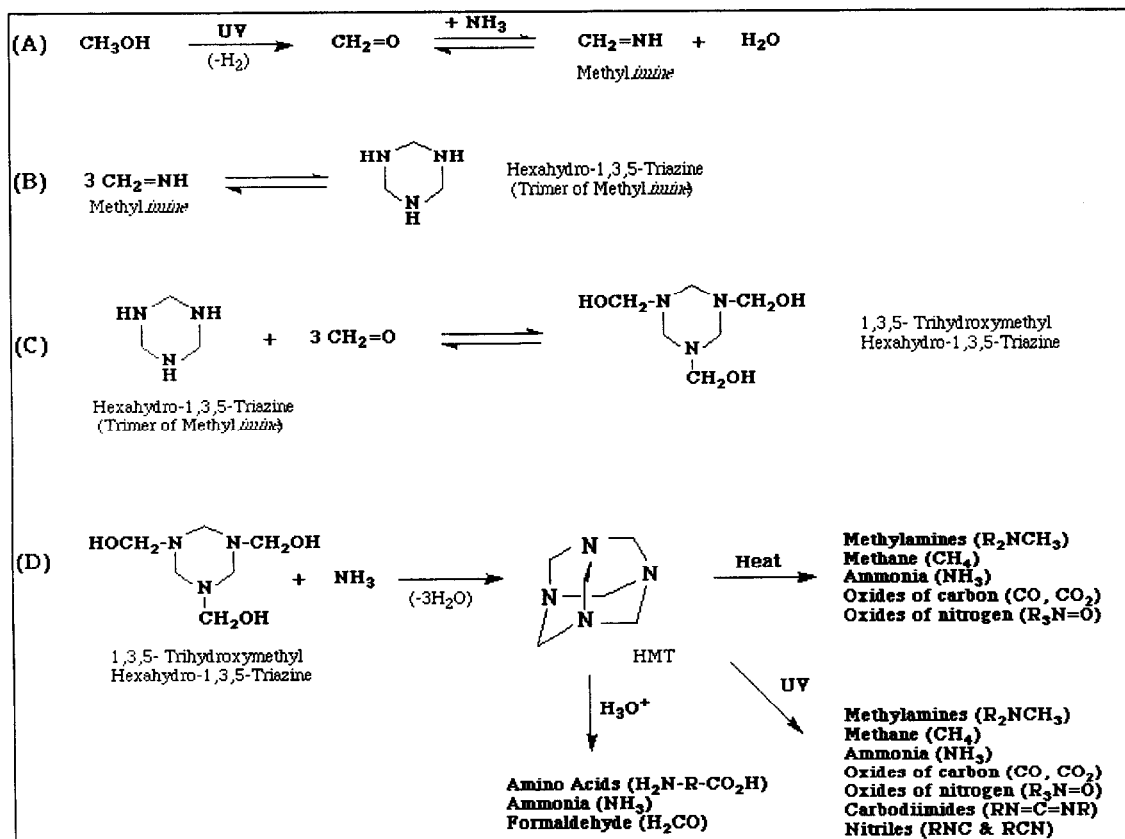


Fig. 5. HMT chemistry. From Bernstein et al. 1995—courtesy of M. Bernstein.

although it is well known in the gaseous phase (Mauersberger et al., 1992). In comet Halley, HMT has been evoked to explain the low NH_3 abundance observed in the coma (Kargel, 1992), but it has not been detected to date.

A scheme of HMT production is shown in Fig. 5. Formaldehyde is produced by methanol UV oxidation. It then reacts with ammonia to produce methylimine and its trimer: hexahydro-1,3,5-triazine. Successive reactions with formaldehyde and ammonia result in the formation of HMT (Bernstein et al., 1995). Such a mechanism explains why it is only a minor product in the Briggs et al. experiments with ices of $\text{H}_2\text{O}:\text{CO}:\text{NH}_3$. Methanol plays a key role and it has been shown by ^{13}C isotopic substitution that it is the source of HMT's carbon.

HMT photolysis in an argon or water matrix produce nitriles (RCN) and isonitriles (RNC) (Bernstein et al., 1994). Knowing this, it is interesting to note that it has been shown that the CN radical might have an extended source in comet Halley (Klavetter and A'Hearn, 1994). According to these authors, this source could be large molecules present on grains because the observed HCN cannot explain the amount of CN in comets (Crovisier and Schloerb, 1991). Nevertheless, this was not the case for large heliocentric distances (> 2.9 AU) in comet Hale-Bopp (Rauer et al., 1997). Possibly, it was because the

grains were too cold and not irradiated enough to release refractory material (Crovisier, 1998). For smaller heliocentric distances, morphologies of HCN and CN do not match, which implies another parent molecule for CN (Woodney et al., 1998). But the other observed CN-containing compounds (HNC, CH_3CN , HC_3N) are only minor products and cannot explain the discrepancy.

Thus, having been produced in the interstellar ices, as we have just seen, HMT could act as a 'grandmother' molecule for the CN extended source: $\text{HMT} \rightarrow \text{RCN} \rightarrow \text{CN}$. As yet, there has been no observation of HMT in comets. If present, its detection would be masked by the Si–O and C–O vibration bands that are in the same region as the strongest HMT infrared signatures (Bernstein et al., 1995).

5.3. Thermal processing of ices

Polyoxymethylene, and associated molecules and polymers, have been detected in the same experimental setup, where several mixtures containing formaldehyde and ammonia, instead of being irradiated, were warmed slowly to room temperature. The presence of ammonia, if only in small amounts (0.5%) is necessary for the formation of POM (Schutte et al., 1993a,b).

There are many differences between the organics

detected with or without UV processing of ices. Without irradiation, HMT is not detected, which is quite surprising as H_2O and NH_3 readily react in the gaseous phase to form HMT (Bernstein et al., 1995; Walker, 1964). Likewise, ketones, amides or esters, easily synthesized under irradiation, are quite rare in those experiments. It seems that UV photons provide enough energy to surmount the energy barrier for formation of these molecules. Without UV, POM's production is favored since it requires less energy.

5.4. Irradiation by charged particles

Bernstein et al. (1995) have suggested that irradiating a mixture of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3$, with charged particles, would not lead to the formation of HMT. Indeed, rather than a conversion of CH_3OH into H_2CO that is the first step toward HMT formation, acetone is synthesized. The main compound of the residue would then be the polyaminomethylene: $(-\text{CH}_2-\text{NH}-)_n$, PAM. This molecule has not yet been identified in any experimental simulation, but Moore et al. (1996) have detected acetone after irradiating a $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ mixture with 1 MeV protons.

Important work concerning the particle bombardment of ices has been performed by Strazzulla's team in Catania. The experimental setup is shown in Fig. 4c. The particles used are H^+ , He^+ , N^+ or Ar. The bombardment of a large diversity of carbon containing ices induces an evolution toward an amorphous material called: Ion Produced Hydrogenated Amorphous Carbon (IPHAC) (Strazzulla, 1997; Strazzulla and Baratta, 1991; Strazzulla et al., 1991a).

The general results are the following: up to a dose of about 10 eV/C-atom the ice is partially converted into a refractory material. From 10–25 eV/C-atom, a massive loss of H is observed and the target evolves to an organic material made of chemical chains of different sizes. For stronger irradiations (≥ 25 eV/C-atom) IPHAC, the ultimate state of organic degradation, is formed (Strazzulla, 1997). It has been shown by Jenniskens et al. (1993) that energetic UV (10 eV) irradiation of the organic residue of processed ices also leads to IPHAC formation which then can be also called: Irradiation Produced Hydrogenated Amorphous Carbon. Thus, after a typical lifetime in the interstellar medium, UV radiation and/or particles convert the organic mantle of interstellar dust into amorphous hydrogenated carbon.

We note that in these kinds of experiment, C_3O_2 , which is sometimes evoked as an extended source of CO, has been detected after irradiation of ices containing CO or CO_2 (Brucato et al., 1997a; Moore et al., 1991).

From an exobiological point of view, the works of Kobayashi et al. (1995) and Kasamatsu et al. (1997) have been very productive. Their experimental setup is presented in Fig. 4d. After an irradiation, by 3 MeV protons,

of mixtures containing water, ammonia and a carbonated molecule (carbon monoxide, methane or propane), they detected by HPLC several amino acids: glycine, and for the first time in a cometary simulation, alanine, aminobutyric acid and aminoisobutyric acid. These new detections were not made directly from the organic residue, but after an acid-hydrolysis in water. Unhydrolyzed residues gave only a trace of glycine whose detection has already been reported by Briggs et al. (1992) without any liquid water introduced to the analysis protocol. One can deduce from these results that, except glycine, no amino acids are likely to be present in the dry environments of comets or dust particles, but there are chemical precursors that react in the presence of liquid water to produce them.

A large diversity of organic compounds after an experimental simulation have been reported by McDonald et al. (1996). Alkanes, ketones, esters and other molecules have been detected by GC-MS. The composition of the initial mixture is $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}_2:\text{C}_2\text{H}_6$ (80:16:3.2:0.8). Ices are irradiated at 77 K in a helium plasma induced by a Tesla coil. The temperature is rather different than in interstellar molecular clouds (10 K), but according to the authors it should not be a problem as it has been shown that $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ices, deposited at 10 K and warmed up, undergo few modifications up to 120 K (Blake et al., 1991). H_2CO has not been detected, whereas it is easily synthesized by UV processing of similar ices. It is stated in the paper that formaldehyde could be a signature of UV irradiation of the ice. We suggest that their non-detection of H_2CO arises from the absence of CO in their mixture: formaldehyde has been detected in notable amounts after irradiation of $\text{H}_2\text{O}:\text{CO}$ ices by protons (Moore et al., 1991) but was not noticeable in $\text{H}_2\text{O}:\text{CO}_2$ (Brucato et al., 1997b; Moore et al., 1991) despite a previous detection in such mixtures by Pirronello et al. (1982). CO is too volatile to condense at 77 K and this experiment cannot really simulate the pre-cometary and cometary chemistry, as CO is one of the most abundant molecules detected in the coma.

This chapter cannot be concluded without discussing the relevance of experimental simulations. Of course, an irradiation of few hours cannot reproduce billions of years of slow evolution with complex heterogeneous chemistry in an interstellar environment that will never be reproduced in the laboratory. Nevertheless, in the 3.4 μm region, infrared spectra of methane and butane mixtures after a particle irradiation present a very good fit with the observations of dust particles in the diffuse interstellar medium (i.e. highly processed material), and even with spectra of residues from the Murchinson Meteorite (Pendleton et al., 1994). The same results have been obtained with residues of $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{CH}_4/\text{C}_2\text{H}_2/\text{CH}_3\text{OH}$, which have been exposed to direct solar UV radiation on the EURECA space station (Greenberg and Li, 1997; Greenberg et al., 1995). These are also

highly processed materials. Thus Strazzulla's IPHAC appears to be similar to the refractory mantle of dust grains in the harsh conditions of diffuse interstellar medium. The less processed mantle formed in molecular clouds is almost certainly composed of the large range of molecules detected after experimental simulations, with abundances of some characteristic molecules depending on the history of the grain and the contribution of energy sources: UV irradiation \rightarrow HMT, thermal process \rightarrow POM-like polymers, charged particles \rightarrow PAM if it is effectively formed (Fig. 6). But direct observations of dust particles in molecular clouds are difficult because light is totally absorbed. Nevertheless, recent ISO observations of ices in protosolar objects are consistent with cometary observations (Ehrenfreund et al., 1997).

Data drawn from these simulations are necessary for the preparation of space missions to comets. A good illustration of this point is the selection and calibration in our laboratory of chromatographic columns for the COSAC experiment (ROSETTA mission—ESA) and the CHARGE experiment (DS4 mission—NASA) that require an anticipation of the nature of the molecules to be searched for. The preparation of these experiments is based on the review presented here.

6. Summary and future investigations

In this paper, we have shown the association of the chemical composition of comets and their own history, how it is linked to the history of our solar system, and to the importation of molecules required for the emergence of life on Earth: water and prebiotic compounds.

To date, 26 stable molecules (i.e. we do not take into account ions and radicals) have been unequivocally detected in cometary comae. Thanks to experimental simulations and the MS-inferred molecules by Kissel and Krueger (1987), the working basis for the preparation of in-situ experiments is raised to more than a hundred compounds. Among them are volatile molecules which can be directly detected in the coma, and more refractory compounds which are probably decomposed by heating

or photodegradation when the comet becomes active close to the Sun. The links between these molecules have to be investigated in further detail and some could explain extended sources already detected (CN, H_2CO). But the lack of important physico-chemical data leaves many questions open; for example, whether POM's photodegradation can explain the formaldehyde's extended source or not. Moreover such a study is necessary to connect direct measurements on the nucleus by the Rosetta Lander, and remote observations in the coma by the Orbiter.

To study the photodegradation of solid molecules in cometary environments, we have developed, in our laboratory, a reactor in which high molecular weight compounds are irradiated in the far UV under vacuum. The photodegradation products are detected in the gaseous phase by MS or infrared spectroscopy. This is the experience SEMAPHORE Cometaire (Cottin et al., 1999). We plan to obtain qualitative information about the photodegradation products of compounds like POM and HMT in the far UV, as well as quantitative data on quantum yields of production at different wavelengths. These results will be applied to observations and models of cometary environment.

A synergy between in-situ observations, remote sensing, numerical models and experimental simulations is necessary to advance our knowledge of cometary chemistry.

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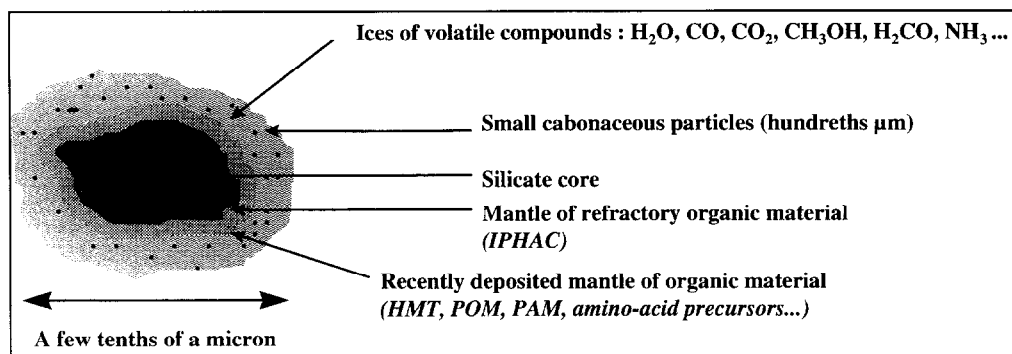



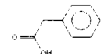


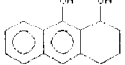





Fig. 6. Suggestion for a dust grain composition from laboratory experiments.

Appendix A

Compound	Initial Ices Mixture				
Hydrogen Peroxyde H_2O_2	H_2O (19)	Hydrazine N_2H_4	NH_3 (19)		
Carbon Monoxide CO	H_2CO (19)	CH_3OH (19)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (4)(8)		
	$\text{H}_2\text{O} : \text{CO}_2$ (12)(15)	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{H}_2\text{O} : \text{C}_2\text{H}_2$ (17)
	CO_2 (12)				
Carbon Dioxide CO_2	$\text{H}_2\text{O} : \text{CO}$ (4)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (4)(8)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (4)(5)(6)(8)(9)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO} : \text{C}_2\text{H}_2/\text{C}_6\text{H}_6$ (4)	H_2CO (19)
	CH_3OH (19)	CO (13)	$\text{H}_2\text{O} : \text{CO}$ (15)	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)
	$\text{H}_2\text{O} : \text{C}_2\text{H}_2$ (17)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{CO} : \text{N}_2$ (13)		
Formaldehyde H_2CO	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3 : \text{CO}_2$ (1)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (4)(5)(6)(8)(9)	$\text{H}_2\text{O} : \text{CO} : \text{N}_2$ (9)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO} : \text{C}_2\text{H}_2/\text{C}_6\text{H}_6$ (4)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (4)(8)
	$\text{H}_2\text{O} : \text{CO}$ (4)	CH_3OH (19)			
	$\text{H}_2\text{O} : \text{CO}$ (15)	$\text{H}_2\text{O} : \text{CO}_2$ (20)	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)	$\text{H}_2\text{O} : \text{CH}_4$ (17)
Methane CH_4	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (4)(5)(6)(8)(9)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (4)(8)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO} : \text{C}_2\text{H}_2/\text{C}_6\text{H}_6$ (4)		
	$\text{H}_2\text{O} : \text{CO}$ (15)	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)		
Ethane C_2H_6	CH_4 (19)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{H}_2\text{O} : \text{C}_2\text{H}_2$ (17)	$\text{H}_2\text{O} : \text{CH}_4 : \text{C}_2\text{H}_2$ (17)	
Ethene C_2H_4	CH_4 (19)	$\text{H}_2\text{O} : \text{CH}_4 : \text{C}_2\text{H}_2$ (17)	Ethyne C_2H_2	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)	C_6H_6 (11)
Propane C_3H_8	CH_4 (19)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)	Allene $\text{H}_2\text{C}=\text{C}=\text{CH}_2$	CH_4 (19)
Methanol CH_3OH	$\text{H}_2\text{O} : \text{CO}$ (15)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{H}_2\text{O} : \text{C}_2\text{H}_2$ (17)	$\text{H}_2\text{O} : \text{CH}_4 : \text{C}_2\text{H}_2$ (17)	
Ethanol $\text{CH}_3\text{CH}_2\text{OH}$	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (8)				
	$\text{H}_2\text{O} : \text{CO}$ (15)	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)	$\text{H}_2\text{O} : \text{CH}_4$ (17)	$\text{H}_2\text{O} : \text{C}_2\text{H}_2$ (17)
	$\text{H}_2\text{O} : \text{CH}_4 : \text{C}_2\text{H}_2$ (17)				
Formic Acid HCOOH	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3 : \text{CO}_2$ (1)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)	Acetone CH_3COCH_3	CH_3OH (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)
Methyl Formate HCOOCH_3	H_2CO (19)	CH_3OH (19)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)		
Cyclopentanone 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (10)	Cyclohexanone 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (10)		
Carbonic Acid H_2CO_3	$\text{H}_2\text{O} : \text{CO}_2$ (12)(15)	CO_2 (12)	Isocyanic Acid HNCO	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3 : \text{CO}_2$ (1)	
Carbon Suboxide C_3O_2	CO (19)	CO_2 (19)	CO (13)	$\text{CO} : \text{N}_2$ (13)	$\text{H}_2\text{O} : \text{CO}_2$ (15)
Formamide NH_2CHO	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3 : \text{CO}_2$ (1)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (8)(9)	Acetamide CH_3CONH_2	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (8)(9)	
Ethylene Glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	$\text{H}_2\text{O} : \text{CH}_3\text{OH}$ (16)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)	
Glycolic Acid HOCH_2COOH	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	Hydroxyacetamide $\text{HOCH}_2\text{CONH}_2$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)
Urea NH_2CONH_2	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	Biuret $\text{NH}_2\text{CONHCONH}_2$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)
Oxamic Acid $\text{NH}_2(\text{CO})\text{CO}_2\text{H}$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	Oxamide $\text{NH}_2(\text{CO})_2\text{NH}_2$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)
Glycerol $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{CO}_2 : \text{C}_2\text{H}_6$ (18)		
Glyceric Acid $\text{HOCH}_2\text{CH}(\text{OH})\text{CO}_2\text{H}$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)	Glyceramide $\text{HOCH}_2\text{CH}(\text{OH})\text{CONH}_2$	$\text{CO} : \text{NH}_3$ (2)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (2)(3)
3-Hydroxypropionic Acid $\text{HOCH}_2\text{CH}_2\text{CO}_2\text{H}$	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (3)		Formamidine $\text{HCNH}(\text{NH}_2)$	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (3)	
Glycine $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (3)	$\text{H}_2\text{O} : \text{CH}_4 : \text{NH}_3$ (14)	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (14)	$\text{H}_2\text{O} : \text{C}_3\text{H}_8 : \text{NH}_3$ (14)	
Ethanolamine $\text{HOCH}_2\text{CH}_2\text{NH}_2$	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (3)		Hexamethylene Tetramine 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (3)	$\text{H}_2\text{O} : \text{CH}_3\text{OH} : \text{NH}_3 : \text{CO}$ (8)(9)
Benzeneacetic Acid 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (10)	Quinoline 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (10)	Indene 	$\text{H}_2\text{O} : \text{CO} : \text{NH}_3$ (10)

1,10-Diol-1,2,3,4-TétrahydroAnthracène 	H ₂ O : CO : NH ₃ (10)	Phenylacetylene 	H ₂ O : CO : NH ₃ (10)	2-Methyl-Naphtalene 	H ₂ O : CO : NH ₃ (10)
Alanine NH ₂ CH(CH ₃)CO ₂ H	H ₂ O : CH ₄ : NH ₃ (14)	H ₂ O : CO : NH ₃ (14)	H ₂ O : C ₂ H ₆ : NH ₃ (14)		
Aminobutyric Acid CH ₃ CH ₂ CH(NH ₂)CO ₂ H	H ₂ O : CH ₄ : NH ₃ (14)	H ₂ O : CO : NH ₃ (14)	H ₂ O : C ₂ H ₆ : NH ₃ (14)		
Aminoisobutyric Acid (CH ₃ NH ₂)(CH ₃)CHCO ₂ H	H ₂ O : CH ₄ : NH ₃ (14)	H ₂ O : CO : NH ₃ (14)	H ₂ O : C ₂ H ₆ : NH ₃ (14)		
POM (-CH ₂ -O-) _n	H ₂ CO : NH ₃ (6)	H ₂ O : H ₂ CO : NH ₃ (6)	CH ₃ OH : H ₂ CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)
	H ₂ O : CH ₃ OH : H ₂ CO : CO : NH ₃ : CH ₄ : CO ₂ : O ₂ (6)	H ₂ CO (19)	H ₂ O : CH ₃ OH : NH ₃ : CO (8)(9)		
HO-CH ₂ -NH ₂ / HO-CH ₂ -O-CH ₂ -NH ₂	H ₂ CO : NH ₃ (6)	H ₂ O : H ₂ CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)	H ₂ O : CH ₃ OH : H ₂ CO : CO : NH ₃ : CH ₄ : CO ₂ : O ₂ (6)
HO-CH ₂ -OH / HO-CH ₂ -O-CH ₂ -OH	H ₂ O : H ₂ CO : NH ₃ (6)	CH ₃ OH : H ₂ CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)	H ₂ O : CH ₃ OH : H ₂ CO : CO : NH ₃ : CH ₄ : CO ₂ : O ₂ (6)	
H ₃ C-CH(OH)-O-CH ₃ / H ₃ C-O-CH ₂ -O-CH(OH)-O-CH ₃	CH ₃ OH : H ₂ CO : NH ₃ (6)	H ₂ CO : CO : NH ₃ (6)	H ₂ O : CH ₃ OH : H ₂ CO : CO : NH ₃ : CH ₄ : CO ₂ : O ₂ (6)		

The following compounds have all been detected in the same experiment : H₂O : CH₃OH : CO₂ : C₂H₆ (18)

Dimethoxymethane (t) CH ₃ OCH ₂ OCH ₃	1,3,5-Trioxane  (t)	Cyclopentane/ Methylcyclobutane C ₅ H ₁₀	Methylpropane C ₄ H ₁₀	Methyl Acetate CH ₃ COOCH ₃	H ₂ O : CH ₃ OH : CO ₂ : C ₂ H ₆ (18)
Hydroxypropanone HOCH ₂ COCH ₃	Butane C ₄ H ₁₀	Pentanol/Méthylpropan ol C ₅ H ₁₂ OH	Methylbutane C ₅ H ₁₂	Methylpropanoate CH ₃ CH ₂ COOCH ₃	
Hydroxybutanone HOCH ₂ CH ₂ COCH ₃	Pentane C ₅ H ₁₂	Methylbutenol (t) C ₅ H ₁₀ OH	Methylpentane C ₆ H ₁₄	Methoxyacetaldehyd e (t) CH ₃ OCH ₂ COH	
Dimethyl ether CH ₃ OCH ₃	Hexane C ₆ H ₁₄	Butanediol C ₄ H ₁₀ (OH) ₂	Methylhexane C ₇ H ₁₆	Acetic Acid (t) CH ₃ COOH	

H₂O : CH₃OH (UV irradiation), H₂O : CH₃OH (Charged particles irradiation), H₂O : CH₃OH (Thermal process)

1 (Hagen et al., 1979) ; 2 (Agarwal et al., 1985) ; 3 (Briggs et al., 1992) ; 4 (Allamandola et al., 1988) ; 5 (Schutte et al., 1991) ; 6 (Schutte et al., 1993) ; 7 (Bernstein et al., 1994) ; 8 (Bernstein et al., 1995) ; 9 (Bernstein et al., 1997) ; 10 (Greenberg and Mendoza-Gomez, 1993) ; 11 (Strazzulla et al., 1991) ; 12 (Brucato et al., 1997b) ; 13 (Brucato et al., 1997a) ; 14 (Kobayashi et al., 1995) ; 15 (Moore et al., 1991) ; 16 (Moore et al., 1996) ; 17 (Hudson and Moore, 1997) ; 18 (McDonald et al., 1996) ; 19 (Gerakines et al., 1996) ; 20 (Pirronello et al., 1982) ;

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